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Ultimate efficiency of polymer/fullerene bulk heterojunction solar cells

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We present model calculations to explore the potential of polymer/fullerene bulk heterojunction solar cells. As a starting point, devices based on poly(3-hexylthiophene) and 6,6-phenyl C_{61}-butyric acid methyl ester (PCBM), reaching 3.5% efficiency, are modeled. Lowering the polymeric band gap will lead to a device efficiency exceeding 6%. Tuning the electronic levels of PCBM in such a way that less energy is lost in the electron transfer process enhances the efficiency to values in excess of 8%. Ultimately, with an optimized level tuning, band gap, and balanced mobilities polymeric solar cells can reach power conversion efficiencies approaching 11%. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2181635]

As the need for renewable energy sources becomes more and more apparent, solar cells are attracting more attention. Organic solar cells based on the bulk heterojunction (BHJ) concept are particularly attractive because of their ease of processing, mechanical flexibility, and potential low cost. Polymer/fullerene BHJs, based on poly(3-hexylthiophene) (P3HT) as the donor and 6,6-phenyl C_{61}-butyric acid methyl ester (PCBM) as the acceptor have reached power conversion efficiencies of 3.5%.[1] Although further improvement of device fabrication has lead to efficiencies of over 4% for this materials combination,[2] efficiencies are not yet high enough for commercial application. Since the incident photon to collected electron efficiency is already high, up to 70% at the absorption maximum of P3HT,[1] it is unclear how much and in which way the efficiency of these devices may be further improved.

As a first approximation Coakley and McGehee predicted that an efficiency of 10% may be within reach.[3] In their calculation it is assumed, among other things, that the fill factor is equal to unity and recombination, either geminate or bimolecular, is neglected. Our ability to accurately model the photocurrent-voltage characteristics of polymer/fullerene solar cells[4] enables us to perform a much more detailed calculation. As a starting point for our investigation we use P3HT/PCBM BHJs. By combining charge carrier mobility measurements[5] with current-voltage measurements performed on illuminated solar cells, we quantitatively model the experimental current-voltage characteristics of our solar cells. The thus obtained theoretical description of P3HT/PCBM solar cells enables us to investigate the enhancement of the efficiency when a number of solar cell parameters is varied. We focus on two effects: First the effect of minimizing the energy loss in the electron transfer from donor to acceptor material is found to be of paramount importance; an efficiency of 8.4% is predicted. Subsequently, the effect of lowering the polymeric band gap is studied. Several research groups have put a lot of effort in the synthesis and application of these polymers.[6–10] At a first glance a low band gap polymer seems beneficial. Due to an improved overlap with the solar spectrum the absorption is enhanced, leading to efficiencies larger than 6%. Surprisingly, we show that once the energy loss in electron transfer is minimized, the best performing solar cell comprises a polymer with a band gap of around 2 eV, clearly not a low band gap. In these cells a lowering of the band gap is accompanied by a decrease of the open-circuit voltage, canceling the benfit of an absorption increase. Ultimately, with energy levels, band gaps and mobilities simultaneously optimized polymer/fullerene solar cells can reach nearly 11% efficiency.

The devices used in this study consist of a blend of P3HT and PCBM sandwiched between a hole-conducting layer of poly(3,4-ethylene dioxythiophene)/poly(styrene sulfonate), approximately of 60 nm thickness, and an evaporated lithium fluoride (1 nm)/aluminum (100 nm) top electrode. After fabrication the devices were annealed at 110 °C for 4 min. All electrical measurements were performed under an inert (nitrogen) atmosphere and a white light halogen lamp set to approximately 1 kW/m^2 was used to illuminate the devices. Figure 1 shows the current density under illumination (J_L) as a function of applied bias (V_a) of a P3HT/PCBM solar cell. To describe the current-voltage characteristics of polymer/fullerene solar cells we have developed a numerical model,[4] including drift and diffusion of charge carriers, the effect of space charge on the electrical field, and a field and temperature dependent charge carrier

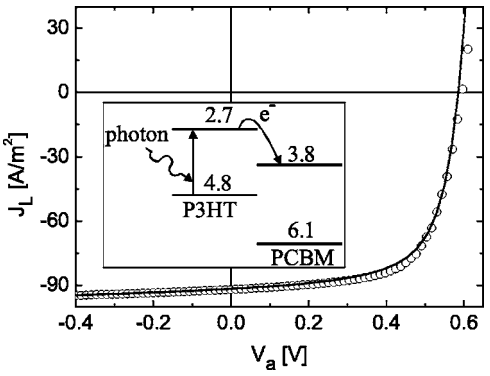

FIG. 1. The current-voltage characteristics of a P3HT/PCBM bulk heterojunction solar cell (symbols) and the fit to the data (line). Used parameters are: active layer thickness 97 nm, relative dielectric constant 3.4, electron mobility 2.0×10^{-7} m^2/V s, hole mobility 1.5×10^{-8} m^2/V s, electron-hole pair generation rate 7.17×10^{27} m^{-3} s^{-1}. The inset shows the energy levels, energies given in electron-volts with respect to vacuum, of a P3HT/PCBM BHJ, together with the process of electron transfer from P3HT to PCBM.

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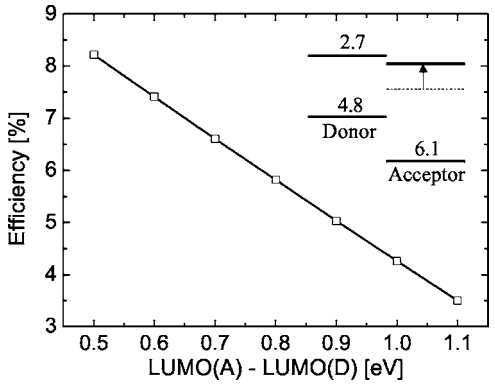

FIG. 2. The influence of the offset between the LUMO of the donor and the acceptor (symbols), the line is drawn as a guide to the eye.

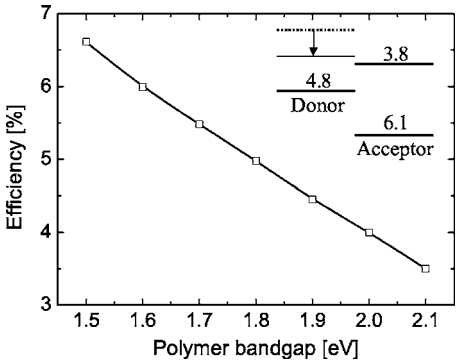

FIG. 3. The influence of the band gap of the polymer on device efficiency (symbols). The line is drawn as a guide to the eye.

generation rate.[11] This model consistently describes, e.g., the light intensity dependence of the open-circuit voltage[12] and the short-circuit current,[13] the field and temperature dependence of the photocurrent,[4,11] and the compositional dependence of the device performance.[14]

Due to the high exciton binding energy in conjugated polymers, light absorption does not lead directly to free charge carriers, but an exciton is created. By mixing in an electron acceptor, it becomes energetically favorable for the electron to jump over to the acceptor, thus breaking up the exciton. This process yields a Coulombically bound electron-hole pair which may dissociate thermally, possibly aided by an electric field.[11] The inset of Fig. 1 shows the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) of P3HT and PCBM. Due to the large offset between the LUMO of the donor, LUMO(D), and the LUMO of the acceptor, LUMO(A), electron transfer from the donor onto the acceptor takes place, thereby breaking up the exciton. However, the excess energy of the electron and the hole is dissipated quickly. This energetic loss is reflected in the open-circuit voltage (V_{oc}), which is limited by the difference between the HOMO of the donor and the LUMO of the acceptor.[12,15] Concomitantly, the LUMO(A)-LUMO(D) offset reduces the output power (and, hence, efficiency) of the solar cell. Experimental and theoretical investigations of polymer/polymer BHJs show that electron transfer occurs provided that the difference in LUMO levels is larger than the binding energy of the intrachain exciton,[16] which is known to be approximately 0.4 eV.[17] Since the difference in LUMO levels is much larger than the exciton binding energy, it should be possible to decrease the LUMO(A)-LUMO(D) offset without decreasing the electron transfer efficiency and thereby increasing the energy difference between the HOMO of the donor and the LUMO of the acceptor. Figure 2 shows the influence of the LUMO(A)-LUMO(D) offset on the device efficiency when all other parameters are kept the same as for the P3HT/PCBM device. The performance of the photovoltaic devices is greatly enhanced by lowering the LUMO(A)-LUMO(D) offset, primarily caused by an increase in open circuit voltage. For the P3HT/PCBM system, the LUMO(A)-LUMO(D) offset amounts to 1.1 eV, leading to 3.5% efficiency. To be on the safe side, the LUMO(A)-LUMO(D) offset is not lowered below 0.5 eV, although Brabec *et al.* have shown that efficient charge transfer takes place in a low band gap polymer/fullerene device with a LUMO(A)-LUMO(D) offset of only 0.3 eV.[8] Ultimately, by lowering this offset to 0.5 eV the device efficiency would increase to more than 8%, showing the great importance of matching the electronic levels of donor and acceptor.

Since P3HT has a relatively high band gap (2.1 eV), improvement of the overlap of the absorption spectrum of the materials used with the solar spectrum may also increase device performance. We study the effect of lowering the polymer band gap by shifting the P3HT part in the absorption spectrum of a P3HT/PCBM blend film down in energy. Hence, we take a realistic absorption spectrum for the polymer, both in shape and in magnitude and do not make the assumption that all the above band gap photons are absorbed and contribute to the photocurrent. The HOMO level of the polymer phase is taken constant, so the open-circuit voltage is not affected by the decrease in band gap, and the energy levels of PCBM remain unchanged. Subsequently, the resulting increase in absorption is calculated and the exciton generation rate is modified accordingly. By using this as input in our simulation, together with the parameters obtained in fitting the current-voltage data of the real P3HT/PCBM device (see Fig. 1), we calculate the resulting device efficiency, see Fig. 3. Clearly, the device performance benefits from lowering the band gap, ultimately reaching 6.6% for a 1.5 eV band gap. The band gap is not lowered beyond 1.5 eV, which corresponds to a LUMO(A)-LUMO(D) offset of 0.5 eV, to ensure efficient electron transfer from the polymer to PCBM. The increase in performance is accounted for by enhancement of the short-circuit current. This calculation shows that the effect of only tuning the LUMO(A)-LUMO(D) offset is more beneficial than only lowering the polymeric band gap.

As a next step the combined effect of lowering the band gap of the polymer and tuning the LUMO(A)-LUMO(D) offset to 0.5 eV is studied, see Fig. 4. For a band gap of 1.5 eV the efficiency amounts to 6.6%, corresponding to the maximum of Fig. 3. However, when the band gap is increased the now fixed LUMO(A)-LUMO(D) offset leads to an increase of the open-circuit voltage, therebye enhancing the efficiency in spite of the reduced absorption. As shown before in Fig. 2, the efficiency corresponding to a 2.1 eV band gap is more than 8%. However, the efficiency shows a broad maximum with the optimal band gap in between 1.9 eV and 2.0 eV, reaching an ultimate efficiency of 8.6%. Surprisingly, the optimal band gap when LUMO(A)-LUMO(D) tuning is employed is very close to the present P3HT value of 2.1 eV, demonstrating that the usage of low band gap polymers is

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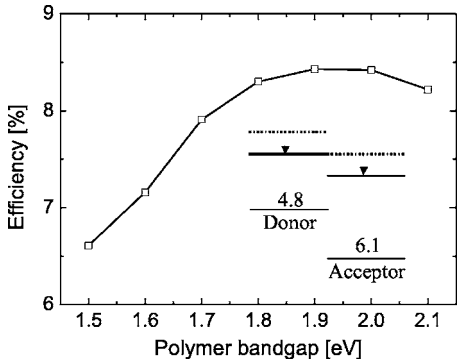

FIG. 4. The combined effect of tuning the LUMO(A)-LUMO(D) offset to 0.5 eV and changing the polymer band gap (symbols). The line is drawn as a guide to the eye.

not the most efficient way of increasing the performance.

The thickness of current polymer/fullerene BHJs is limited by the rather low hole mobility of the polymer phase as compared to the electron mobility of the fullerene. On the other hand, device performance is expected to be enhanced by a thicker active layer since more light is absorbed. Therefore, we study the effect of increasing the hole mobility up to the value for the electron mobility, i.e., 2.0×10^{-7} m^2/V s, in combination with a polymeric band gap of 1.9 eV and a LUMO(A)-LUMO(D) offset of 0.5 eV, corresponding to an optimal situation. A 97 nm thick device with these specifications would yield an efficiency of 9.2%. In order to vary the active layer thickness, it is necessary to recalculate the volume generation rate of electron-hole pairs. From the absorption coefficient we calculate the absorption at each wavelength, taking into account the reflection of the aluminum electrode. By integrating this over the AM1.5 spectrum, we get the relative value for the generation rate.[5] By performing this calculation for various layer thicknesses, we can estimate the resulting efficiency. We note that this is a simplified procedure and it would be more accurate to incorporate optical interference effects in the device,[18] however, we found that the inclusion of an absorption profile as found by Hoppe *et al.* influences the outcome by less than 0.2%. The maximum efficiency of 10.8% is predicted for a layer thickness of 200 nm, showing the great potential of polymer/fullerene based solar cells.

In conclusion, we have shown that the device efficiency of P3HT/PCBM bulk heterojunction solar cells would greatly benefit from tuning of the LUMO level of PCBM in such a way that the LUMO(A)-LUMO(D) offset would be 0.5 eV. In that case the efficiency could be as high as 8%. Another, much pursued, way to increase the performance is to increase the amount of photons absorbed by the film by lowering the band gap of the polymer. Our model calculations confirm that this would indeed enhance the performance. However, the best efficiency is reached when both effects are combined, i.e., favourable LUMOs of both donor and acceptor and tuning of the polymeric band gap. The optimal band gap lies rather close to the present value, however. This indicates that, although lowering the polymeric band gap enhances the efficiency, it would be more benefical to either lower the LUMO of PCBM or find another acceptor with a more favourable LUMO level combined with good charge transporting properties. Ultimately, with balanced charge transport, polymeric solar cells can reach power conversion efficiencies of 10.8%.

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